



Activation by pretreatment of Ag–Au/Al₂O₃ bimetallic catalyst to improve low temperature HC-SCR of NO_x for lean burn engine exhaust



Pavan M. More^{a,b}, Duy L. Nguyen^c, Pascal Granger^c, Christophe Dujardin^c, Mohan K. Dongare^{a,d}, Shubhangi B. Umbarkar^{a,b,*}

^a CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

^b Academy of Scientific and Innovative Research, CSIR, Anusandhan Bhawan, New Delhi 110 001, India

^c Unité de Catalyse et de Chimie du Solide – UMR CNRS 8181, Université Lille1, Sciences et Technologies, Cité Scientifique – Bâtiment C3, 59655 Villeneuve d'Ascq Cedex, France

^d Moji Engineering Systems Ltd., 15-81/B, MIDC, Bhosari, Pune 411026, India

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ABSTRACT

Bimetallic Ag–Au/Al₂O₃ catalyst was synthesised by successive impregnation of 1% Au and 1% Ag on in-house prepared high surface area alumina (450 m²/g). The corresponding monometallic catalysts were also prepared by loading 1% Ag or 1% Au on the same high surface area alumina for comparison. The catalysts were characterised by various physico-chemical techniques and tested for SCR activity under lean burn engine exhaust conditions. Ag–Au/Al₂O₃ catalyst prepared by successive impregnation method showed considerably higher NO reduction (100%) to N₂ compared to 1% Au/Al₂O₃ (70%) whereas the activity was comparable with that of 1% Ag/Al₂O₃ (96%). The effect of various pretreatments on SCR activity of Ag–Au/Al₂O₃ was studied and pretreatment at 250 °C in flow of hydrogen was found to give the best results with 100% NO conversion to N₂ at 353 °C. Further ageing of the catalyst under reaction feed at 500 °C resulted in considerable increase in low temperature activity of bimetallic catalyst with ~40% NO conversion at 222 °C. Even though the SCR activity of pretreated Ag–Au/Al₂O₃ and Ag/Al₂O₃ were comparable, after ageing the Ag–Au/Al₂O₃ showed significantly higher NO conversion (95%) compared to Ag/Al₂O₃ (83%) and Au/Al₂O₃ (70%). The formation of H₂ and CO due to steam reforming of higher hydrocarbon (decane) was evidenced at the temperature of highest deNO_x activity. Detailed investigation of the textural properties of the pretreated and aged catalysts showed presence of well dispersed metallic Au and Ag^{δ+} clusters after pretreatment in hydrogen at 250 °C.

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1. Introduction

The selective catalytic reduction (SCR) of NO_x using hydrocarbon (HC-SCR) is considered as the most promising alternative technology for removal of NO_x from automobile engine exhaust, operating under lean condition to overcome the drawbacks associated with other deNO_x technologies such as urea SCR and lean NO_x trap (LNT). Development of suitable catalysts for HC-SCR of NO_x is an active area of research in academic as well as industrial laboratories. Among the various catalyst compositions investigated for HC-SCR

of NO_x, Ag/Al₂O₃ (2 wt% Ag loading) has shown promising results and is being considered as a potential catalyst for HC-SCR of NO_x for diesel engine exhaust. However Ag/Al₂O₃ catalyst is not efficient for practical application at lower temperature of diesel engine exhaust. The improvement in low temperature deNO_x activity of Ag/Al₂O₃ catalyst is being investigated by varying the catalyst composition and the method of preparation [1–5].

Supported gold catalysts have also been investigated for HC-SCR of NO_x [6,7]. Ueda and Haruta [8] and Haruta and colleagues [9] have studied gold supported on various metal oxides for HC-SCR of NO_x and showed higher NO_x conversion to N₂ on Au/Al₂O₃ in presence of moisture and oxygen [8,9]. Typically alkanes, alkenes [8–11] or CO were used as reductant previously for HC-SCR on Au/Al₂O₃ [12,13]. Ilieva et al. [12,13] have recently reported reduction of NO_x by CO with 100% selectivity to N₂ at 200 °C over

* Corresponding author at: CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India. Tel.: +91 2025902044; fax: +91 2025902633.

E-mail address: sb.umbarkar@ncl.res.in (S.B. Umbarkar).

Au/CeO₂–Al₂O₃. However, the catalytic activity of Au/Al₂O₃ was lower than Ag/Al₂O₃ catalyst.

To improve the catalytic activity of Ag/Al₂O₃, the modification of either support or active component of the catalyst has been attempted before [14–17]. There have been previous attempts on the use of bimetallic catalyst for enlarging the temperature windows of maximum SCR activity. He and Yu [18] modified Ag/Al₂O₃ with Pd which showed higher SCR activity compared to Ag/Al₂O₃ in temperature range of 300–450 °C. The catalytic activity has been related to the formation of more enolic species on Ag–Pd/Al₂O₃ compared to Ag/Al₂O₃. Arve et al. [14] reported the SCR activity of bimetallic nano gold and silver with varying silver and gold loading on alumina and titania. Bimetallic catalyst showed only 30% NO conversion at 500 °C which was lower compared to Au/Al₂O₃ (~45%). Recently we have reported the SCR activity of Au/Al₂O₃ (1 wt% Au) prepared by deposition precipitation method. However, the catalytic activity of Au/Al₂O₃ was found to be lower than in-house prepared Ag/Al₂O₃ (2 wt% Ag) catalyst [19]. The gold-based catalysts exhibited good resistance to thermal ageing which could certainly be adapted to bimetallic formulations. As a general trend, a complex surface chemistry takes place both on gold and silver based catalysts which involve the metal and the support [20]. It was previously found that the extent of metal/support interface and optimal ratio of electrophilic to metallic Au or Ag species govern the overall performances in terms of activity and selectivity toward N₂ production [20–22].

Hence to further improve the low and high temperature activity of Ag/Al₂O₃ catalyst system, we have prepared 1% Ag–1% Au/Al₂O₃ catalysts by successive impregnation method and tested for SCR of NO_x. The effect of different pretreatments on SCR activity of the bimetallic catalyst has been investigated in order to optimise the surface properties regarding the above-mentioned parameters which influence the catalytic activity. Catalytic properties are compared to extended bulk and surface characterisation using various physico-chemical techniques for subsequent comparisons.

2. Experimental

2.1. Catalysts preparation

Chemicals and reagents: AgNO₃ (99.8 wt%, Thomas Baker) and HAuCl₄ (49 wt% Au, LOBA Chemie) were used without further purification.

Alumina (γ -Al₂O₃) support was prepared by sol–gel method by dissolving 248.96 g aluminium tri-sec-butoxide (97%, Aldrich) in 300 g isopropanol followed by dropwise addition of isopropanol solution (50 mL) of NH₄OH (5 mL, 25%) with constant stirring till formation of the semitransparent gel. Gel was dried in air for 12 h, and calcined at 500 °C for 4 h and further used as support for preparation of all the catalysts in present work.

1 wt% Au/Al₂O₃ catalyst was prepared by deposition precipitation method using urea. A slurry of γ -alumina (9.9 g) in water (700 mL) was heated at 80 °C with dropwise addition of gold(III) chloride solution (0.204 g HAuCl₄ in 10 mL H₂O) with constant stirring. Urea solution (250 mL 10 M aqueous solution) was added dropwise to the above solution. The obtained sample was aged for 12 h, then filtered and washed with water till complete removal of chlorides and dried at 80 °C for 12 h. The solid was then calcined at 500 °C for 6 h and labeled as AuAl.

Wet impregnation method was used to prepare 1 wt% Ag/Al₂O₃ by adding silver nitrate (0.157 g AgNO₃ in 20 mL H₂O) solution to the slurry (700 mL H₂O) of γ -Al₂O₃ (9.9 g) prepared by sol–gel method. The catalyst was dried at 80 °C for 12 h followed by calcination at 500 °C for 6 h and labeled as AgAl.

Bimetallic catalyst 1Ag–1Au/Al₂O₃ was prepared by successive impregnation method. Initially 1 wt% Au/Al₂O₃ was prepared by deposition-precipitation method using urea as mentioned previously (except calcination step). This 1 wt% Au/Al₂O₃ catalyst (dried at 80 °C for 12 h) was further impregnated with AgNO₃ (0.157 g in 20 mL H₂O) solution to get bimetallic 1% Ag–1% Au/Al₂O₃ catalyst. The catalyst was dried at 80 °C for 12 h and then calcined at 500 °C for 6 h and labeled as AgAuAl.

2.2. Catalyst characterisations

2.2.1. Powder X-ray diffraction studies

The powder X-ray diffraction data was collected on a Philips (Xpert) equipped with a Ni filtered Cu K α radiation (λ = 1.5406 Å, 40 kV, 30 mA). The data was collected in the 2θ range 10–80° with a step size of 0.02° and scan rate of 4° min^{−1}.

2.2.2. Nitrogen adsorption studies

The BET surface area of the calcined samples was determined by N₂ sorption at 77 K using NOVA 1200 (Quanta Chrome) equipment. Prior to N₂ adsorption, the material was evacuated at 300 °C under vacuum. The specific surface area, S_{BET} , was determined according to the BET equation.

2.2.3. UV–vis diffuse reflectance studies (UV–vis DRS)

UV–vis DRS spectra were recorded with a UV–vis spectrophotometer PerkinElmer, Lambda 650 with integrating sphere assembly in the diffuse reflectance mode between 200 and 800 nm at a step of 0.2 nm with a slit width of 1 nm. BaSO₄ was used as a reference sample to confirm the baseline spectrum.

2.2.4. X-ray photoelectron spectroscopy study (XPS)

X-ray photoelectron spectroscopy (XPS) was used for the characterisation of surface of pretreated and aged catalysts. XPS experiments were performed using a V. G. Microtech (UK) Unit ESCA 3000 spectrometer equipped with a Mg K α X-ray source ($h\nu$ = 1253.6 eV) and a hemispherical electron analyser. The X-ray source was operated at 150 W. The residual pressure in the ion-pumped analysis chamber was maintained below 1×10^{-9} Torr during data acquisition. Binding energy (B.E.) values were referenced to the binding energy of the Al 2p core level (74.6 eV).

2.2.5. Energy dispersive X-ray spectroscopy (EDS)

The dispersion of metal on the catalyst surface was measured by EDS elemental mapping images taken using Quanta FEI 200 3D equipped with tungsten filament as source of electron.

2.2.6. Transmission electron microscopy (TEM)

TEM experiment was performed with Tecnai FEI G2 microscope, using an accelerating voltage of 300 kV. For TEM analysis, the sample was previously ultrasonically dispersed in isopropanol solvent and then drop of the suspension was deposited on a carbon coated Cu grid of 200 mesh.

2.3. Catalytic activity

The selective catalytic reduction (SCR) of NO_x was carried out at atmospheric pressure using synthetic gas mixture representing realistic exhaust condition of lean engine in quartz tubular down flow reactor (inner diameter 20 mm). Catalyst powder (360 mg) diluted with commercial silicon carbide (2 g) was placed in the reactor and a thermocouple was inserted in the center of the catalyst bed to measure the temperature. Typical reaction feed used for SCR activity was 300 ppm NO, 300 ppm CO, 300 ppm C₃H₆, 2000 ppm H₂, 100 ppm C₁₀H₂₂, 10% CO₂, 10% O₂, 5% H₂O and balance He. The

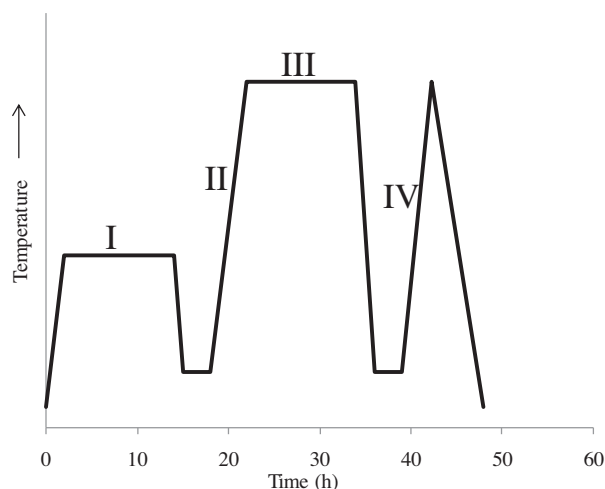


Fig. 1. Typical protocol for catalyst testing.

total flow rate of the gas mixture was adjusted to 300 mL min^{-1} to obtain a gas hourly space velocity of $50,000 \text{ h}^{-1}$.

Fig. 1 illustrates the typical experimental procedure implemented for the catalytic measurements. Initially (Step I) the catalyst was pretreated under different oxidative or reductive atmosphere for 12 h. The different pretreatment conditions used were (i) at 250°C in hydrogen flow (ii) at 500°C in hydrogen flow or (iii) at 500°C in air flow. After pretreatment the catalyst was cooled to 80°C and the reaction feed was passed on catalyst surface with increasing the temperature from 80°C to 500°C with heating rate of 2°C min^{-1} (Step II). The reaction feed was stabilised on the catalyst at 500°C for 12 h for catalyst ageing (Step III). Later the catalyst was cooled to 80°C and in the last stage (Step IV) the catalytic activity was monitored under reaction feed with increasing the temperature from 80 to 500°C with heating rate of 2°C min^{-1} .

The concentrations of the inlet and outlet gases were simultaneously monitored using Micro GC (Varian, CP 4900) and NO_x analyser (Environment SA MIR 9000). The micro GC has two columns to detect different gases: molecular sieves (MS 5 A) for H_2 , N_2 , O_2 , NO and CO and Porapak Q for H_2 , CO_2 , N_2O , C_3H_6 and H_2O .

The NO conversion was calculated from outlet molar flow rates of $\text{N}_2 + \text{N}_2\text{O}$ formation (F_{N_2} , $F_{\text{N}_2\text{O}}$) and inlet molar flow rate of NO (F_0 , NO) using the following Eq. (1):

$$\% \text{NO Conv.} = 100 \times \frac{2 \times (F_{\text{N}_2} + F_{\text{N}_2\text{O}})}{F_{0,\text{NO}}} \quad (1)$$

N_2 selectivity was calculated using following Eq. (2):

$$S_{\text{N}_2} = 100 \times \frac{F_{\text{N}_2}}{F_{\text{N}_2} + F_{\text{N}_2\text{O}}} \quad (2)$$

3. Result and discussion

3.1. Catalytic activity

The catalytic activity of monometallic $\text{Ag}/\text{Al}_2\text{O}_3$ (AgAl) and $\text{Au}/\text{Al}_2\text{O}_3$ (AuAl) catalysts was compared with bimetallic $\text{Ag-Au}/\text{Al}_2\text{O}_3$ (AgAuAl) catalyst during the selective catalytic reduction (SCR) of NO by hydrocarbons. The influence of various thermal pretreatments using bimetallic $\text{AgAu}/\text{Al}_2\text{O}_3$ catalyst (AgAuAl) was investigated. The selectivity for N_2 and N_2O formation as well as the concentration of different reductants during the temperature-programmed reaction was carefully examined.

3.1.1. Catalytic activity of monometallic and bimetallic catalysts

SCR activity of bimetallic AgAuAl catalyst was compared with monometallic AuAl and AgAl catalysts. The NO to N_2 conversion curves of catalysts treated in H_2 at 250°C (Step I) are presented in Fig. 2A. Monometallic AuAl and bimetallic AgAuAl catalysts showed 100% selectivity for N_2 over a complete temperature range whereas AgAl catalyst showed less than 100% selectivity for N_2 up to 275°C with formation of N_2O . A typical volcano-type profile was obtained for NO conversion on AgAl catalyst which was previously ascribed to the involvement of NO_2 as intermediate [20]. The spill-over of NO_2 from the metal to activated hydrocarbon onto the support was proposed by Burch and Watling [23]. The volcano-type curve can be explained by kinetically limited reaction at low temperature (NO conversion to NO_2) whereas thermodynamic unfavourable NO_2 formation at high temperature. The decrease in the NO conversion at higher temperature can also be attributed to unselective oxidation of hydrocarbon contributing to the volcano type curve of NO_x reduction.

At low temperature, the AgAl catalyst showed highest NO conversion whereas AgAuAl catalyst presented marginally lower conversion and AuAl catalyst showed significantly lower NO conversion. The SCR activity of pretreated AgAuAl and AgAl catalysts around 350°C was comparable with maximum NO conversion of 100% and 96%, respectively. However the maximum NO conversion for AuAl catalyst was considerably lower (70%). Above 400°C , AgAuAl and AgAl catalysts exhibited similar conversion curves with decreasing NO conversion with increase in temperature. The three catalysts were then aged overnight under reaction feed before a second temperature-programmed reaction (Step IV

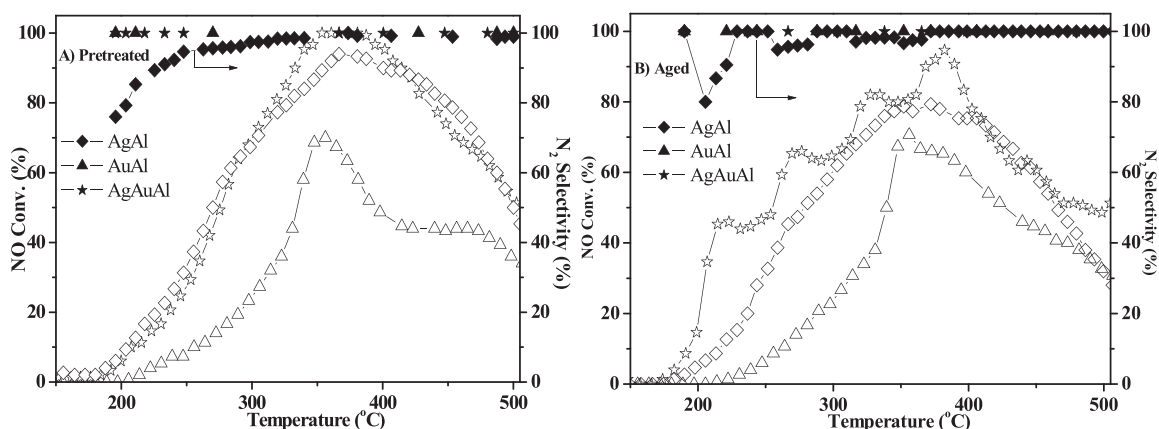


Fig. 2. SCR activity of catalysts after (A) pretreatment at 250°C in H_2 and (B) aged. % NO conversion (open symbols) and N_2 selectivity (filled symbols). Reaction feed: 300 ppm NO , 300 ppm CO , 300 ppm C_3H_6 , 2000 ppm H_2 , 100 ppm $\text{C}_{10}\text{H}_{22}$, 10% CO_2 , 10% O_2 , 5% H_2O , He balance, GHSV = $50,000 \text{ h}^{-1}$.

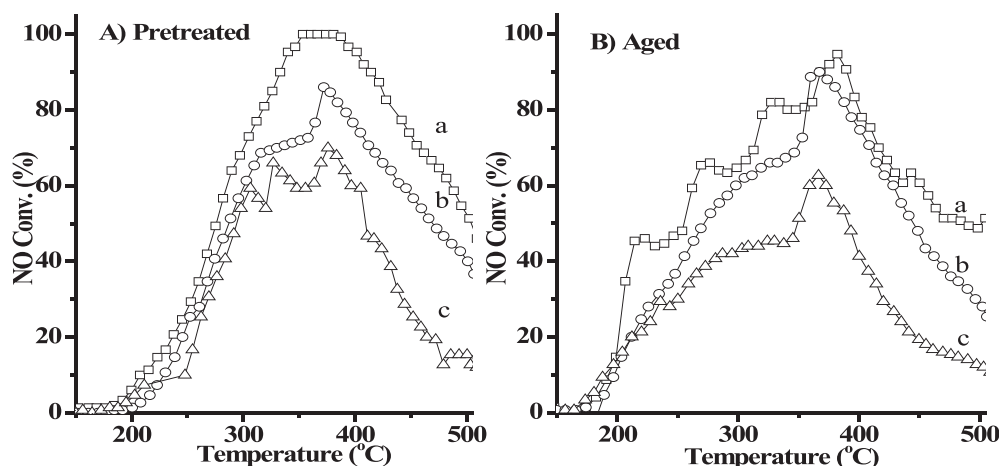


Fig. 3. SCR activity of AgAuAl catalyst (A) after different pretreatments a) 250 °C in H₂, b) 500 °C in H₂, c) 500 °C in air. (B) Aged. Reaction feed: 300 ppm NO, 300 ppm CO, 300 ppm C₃H₆, 2000 ppm H₂, 100 ppm C₁₀H₂₂, 10% CO₂, 10% O₂, 5% H₂O, He balance, GHSV = 50,000 h⁻¹.

– Fig. 1) was carried out. Clearly the catalytic activity (Fig. 2B) was altered after ageing procedure. AgAuAl catalyst had shown improved low temperature activity compared to pretreated catalysts under H₂ at 250 °C. However there was no improvement in low temperature activity for AuAl and AgAl catalysts. After ageing AgAuAl catalyst has shown better low temperature activity (222 °C) with 40% NO conversion compared to AgAl (14%) and AuAl (~2%) catalysts. Higher maximum NO conversion (95%) was obtained on AgAuAl catalyst compared to AgAl catalyst (78%) and AuAl catalyst (70%). There was marginal increase in temperature corresponding to maximum NO conversion after ageing in case of AgAuAl and AgAl catalysts. A decrease in high temperature activity (above 400 °C) was evidenced for AgAuAl and AgAl catalysts. A reverse tendency was observed for AuAl with increase in high temperature activity after ageing which is in agreement with the previous report [21]. Arve et al. reported lower NO conversion on bimetallic Au–Ag/Al₂O₃ catalyst compared to monometallic Au/Al₂O₃ catalyst (45% NO to N₂ conversion at 500 °C) [14]. This difference can be assigned to the presence of hydrogen in the reaction mixture in present study.

3.1.2. Effect of different pretreatments on SCR activity of AgAuAl

The effect of different pretreatments on SCR activity of AgAuAl catalyst is shown in Fig. 3A. AgAuAl catalyst was pretreated under three different conditions; at 250 °C in presence of hydrogen, at 500 °C in presence of hydrogen or at 500 °C in presence of air. Complete selectivity for N₂ was obtained using AgAuAl catalyst over the entire range of temperature irrespective of the thermal pretreatment. The NO conversion was initiated around 200 °C and the catalysts showed almost similar NO conversion profiles up to 300 °C. AgAuAl catalyst pretreated at 250 °C in presence of hydrogen showed maximum activity with 100% NO conversion at 353 °C. Catalyst pretreated at 500 °C in hydrogen showed 86% NO conversion at 372 °C whereas the same catalyst after pretreatment in air at 500 °C showed only 70% NO conversion at 375 °C. Above 400 °C, the NO conversion decreased for catalyst pretreated under different conditions. However the catalyst pretreated under H₂ at 250 °C exhibited highest NO conversion compared to other pretreated catalysts. To our knowledge effect of different pretreatments on SCR activity of bimetallic catalysts has not been reported in the literature. Nam and colleagues [24] underlined the effect of pretreatment in presence of O₂ and H₂+O₂ on reducibility of silver species in Ag/Al₂O₃. The reducibility of Ag species was improved when pretreated in flow of H₂+O₂ compared to only O₂. The reduction of Ag initiated at room temperature with H₂ con-

Table 1

Specific surface area and elemental analysis of Al₂O₃, AgAuAl, AgAl and AuAl catalysts.

Sr. no.	Catalysts	Surface area (m ² /g)	Element wt%	
			Ag	Au
1	γ-Al ₂ O ₃	450	–	–
2	AgAuAl	224	1.04	0.80
3	AgAl	239	0.90	–
4	AuAl	210	–	0.96

sumption maxima at 150 °C when pretreated in H₂+O₂ whereas the catalyst pretreated in only O₂ showed initiation of reduction at 100 °C with H₂ consumption maxima at 350 °C. The pretreatment can affect surface composition of bimetallic AgAuAl catalyst as suggested by catalytic measurements. The stability of the catalytic performances was investigated by ageing the catalyst at 500 °C under reaction feed for 12 h (Fig. 1 Step III). The NO conversion measured on aged catalysts is presented in Fig. 3B. It should be noted that the selectivity for N₂ was not altered (100%) in the whole temperature range studied even after ageing irrespective of the thermal pretreatment. The aged catalysts showed higher activity at low temperature whereas the maximum NO conversion level decreased around 350 °C for all catalysts. The aged catalyst pretreated in hydrogen at 250 °C showed almost 40% NO conversion at 222 °C whereas aged catalyst pretreated in hydrogen and air at 500 °C showed ~24% and ~2% NO conversion respectively. The catalysts pretreated in hydrogen at 250 and 500 °C showed almost similar maximum conversion (90%) at 353 °C whereas catalyst pretreated in air showed only 62% NO conversion at 372 °C. The catalyst pretreated in H₂ at 250 °C showed significant enhancement in SCR activity after ageing as compared to other pretreatments. The comparison of the temperature corresponding to 50% NO conversion (T₅₀) also emphasised the best catalytic performances of the catalyst pretreated under hydrogen at 250 °C with the lowest T₅₀ (250 °C) whereas highest T₅₀ (336 °C) was obtained for the catalyst pretreated at 500 °C under air. The catalyst pretreated at 500 °C under H₂ showed intermediate T₅₀ at 276 °C. In addition the experiments were carried out under steady state conditions (not presented) and the results showed similar NO conversion profiles.

As a general trend, it seems obvious that a pre-reductive thermal treatment prior to SCR reaction has a beneficial effect. However, it depends on the reduction temperature, a moderate pre-reduction temperature seems more appropriate due to possible thermal sintering at high temperature (500 °C). Interestingly, ageing overnight at 500 °C under reaction conditions has two opposite effects related

to slightly lower maximum NO conversion and a significant broadening of the operating window with a significant rate enhancement in NO conversion at low temperature. All those observations reflect significant surface reconstructions during reaction which may depend on the nature of the pre-activation thermal treatment. Indeed, the equilibration of the oxidation state of gold and silver can be of capital importance.

3.1.3. Correlation of NO_x reduction activity with CO, H₂ and propene evolution

In our previous work, the role of hydrogen in activation of NO in the presence of decane, propene and CO were reported on AuAl catalyst [19,21]. The concentration of different reactants like H₂, CO and propene were monitored during temperature-programmed reaction on AgAuAl, AgAl and AuAl catalysts (Figs. 4–6, respectively). In case of AgAuAl catalyst pretreated at 250 °C in H₂ (Fig. 4) a continuous decrease in hydrogen concentration with corresponding increase in NO conversion was observed from 180 °C without considerable change in CO and C₃H₆ concentration upto 230 °C indicating low temperature hydrogen SCR of NO_x. From 230 to 353 °C, marginal increase in CO concentration could be related to activation of decane. A significant formation of hydrogen and CO at 353 °C may be due to the steam reforming of higher hydrocarbon (decane) in the feed [20], whereas decrease in C₃H₆ concentration may be due to propene SCR of NO_x. Concentration of H₂ decreased after 380 °C whereas concentration of CO increased continuously and reached 1300 ppm at 500 °C which correspond to the partial oxidation/reforming of decane (100 ppm) to CO and initial CO content in the feed. However the amount of CO generated does not match with increase in hydrogen concentration when steam reforming of decane is considered. Hydrogen is known to be better reductant compared to CO and C₃H₆ in SCR reaction and is known to help in lowering the temperature of SCR activity [1,19]. The hydrogen generated during steam reforming of decane on AgAuAl catalyst was consumed during SCR activity and hence equivalent

amount of hydrogen could not be observed in the analysis. Pretreated and aged AgAuAl catalyst showed 100% selectivity for N₂ over complete temperature range.

Lee et al. [25] have studied the fuel reforming assisted SCR of NO_x using Ag/Al₂O₃ catalyst where higher hydrocarbon was used for catalytic partial oxidation (CPOX) for generation of CO/H₂ using separate commercial diesel fuel cracking (DFC) catalyst. The study has shown very poor NO_x and hydrocarbon conversion upto 350 °C with the individual hydrocarbons in absence of DFC catalyst whereas in presence of DFC considerable improvement in low temperature (<300 °C) SCR activity was observed. DFC catalyst generates hydrogen *in situ* by partial oxidation of decane which acts as an additional reductant with improved SCR activity below 300 °C [25]. In the present case reforming and SCR activity are observed on the same AgAuAl catalyst and no separate catalyst was required for reforming of the higher hydrocarbon (decane) resulting in improved low temperature SCR activity. However this catalyst was not efficient for the selective reduction of NO_x by CO leading to release of unreacted and formed CO at high temperature.

Interestingly in the case of AgAuAl catalyst aged overnight under reaction feed (Step III – Fig. 1), low temperature H₂-SCR appeared to be more prominent (nearly 40% NO conversion at 222 °C) as seen in Fig. 4B. The concentration of H₂ at 222 °C was significantly lower for aged catalyst (862 ppm) compared to the freshly pretreated catalyst (1547 ppm) which is in agreement with higher NO conversion after ageing. This indicates the broadening of temperature window for NO conversion after ageing. Similar trend was observed for evolution of other reductants on aged catalysts compared to the pretreated catalyst. The concentration of H₂ and propene remain unchanged after ageing except CO. At 500 °C the CO concentration was 967 ppm which could reflect incomplete reforming of decane after ageing. Marginal decrease in both NO conversion and extent of steam reforming indicated slight deactivation of the catalyst during ageing procedure.

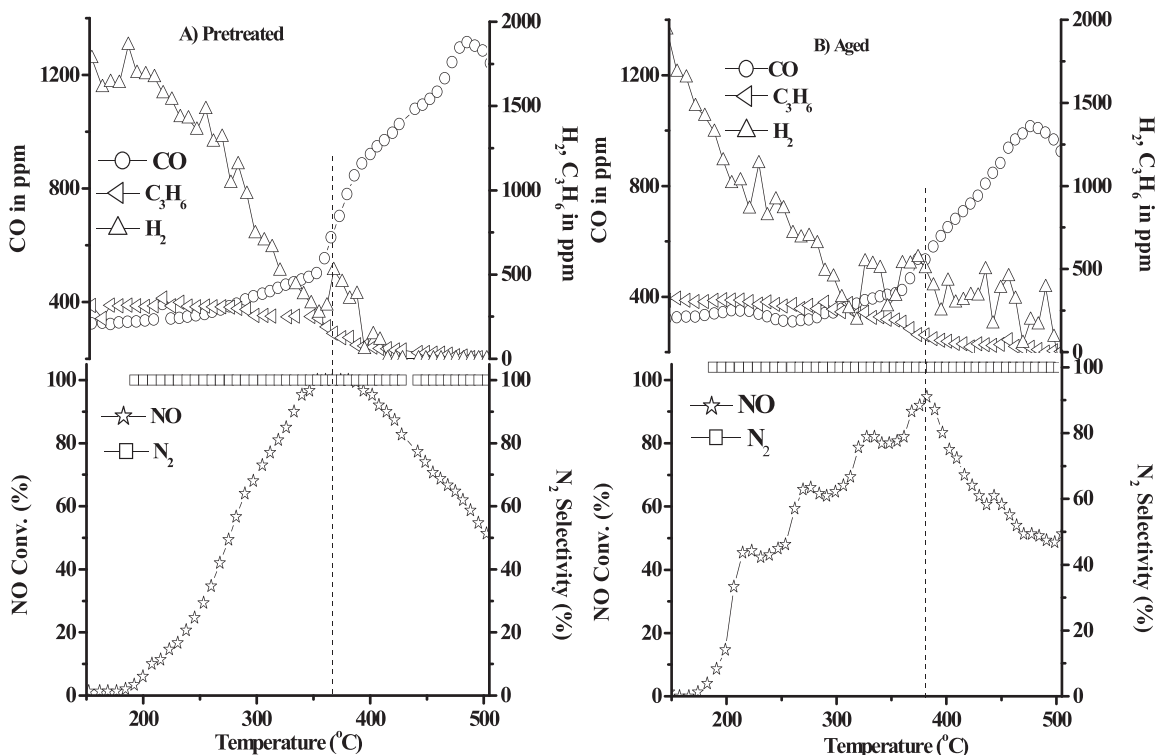


Fig. 4. Change in concentration of CO, H₂ and C₃H₆ during HC-SCR on AgAuAl catalyst A) pretreated in H₂ at 250 °C and B) aged. Reaction feed: 300 ppm NO, 300 ppm CO, 300 ppm C₃H₆, 2000 ppm H₂, 100 ppm C₁₀H₂₂, 10% CO₂, 10% O₂, 5% H₂O, He balance, GHSV = 50,000 h⁻¹.

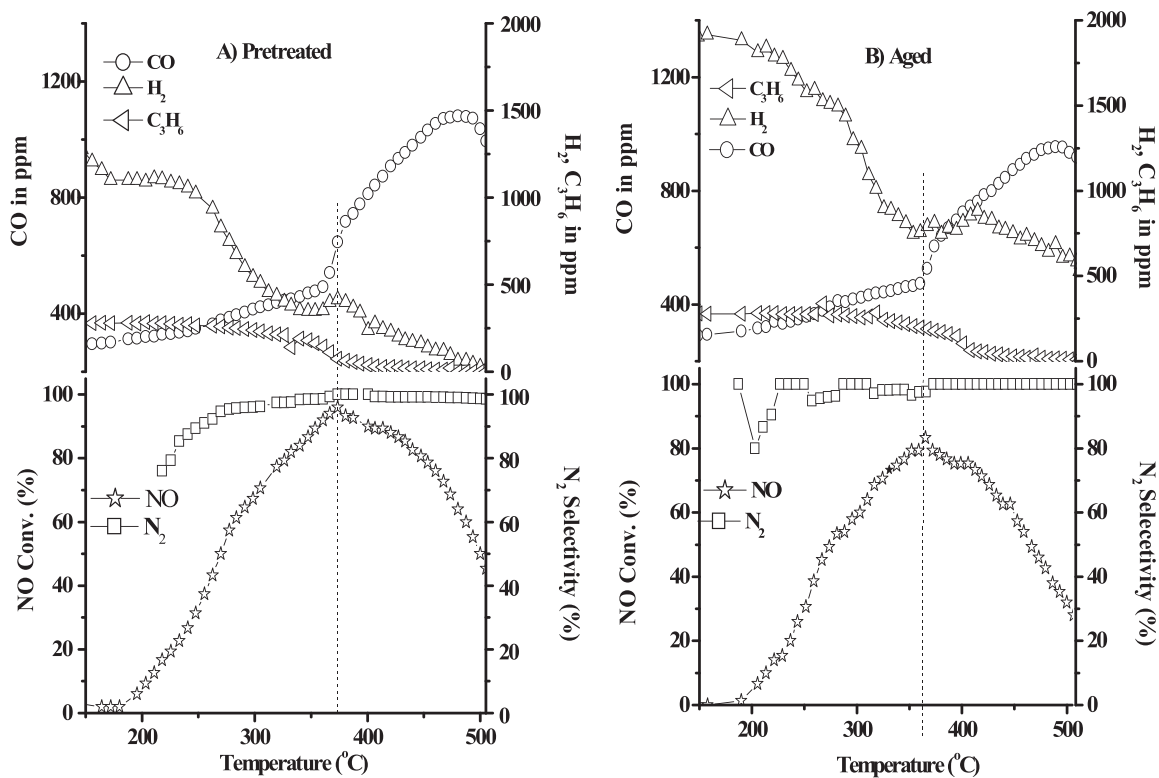


Fig. 5. Change in concentration of CO, H₂ and C₃H₆ and NO_x conversion during HC-SCR on AgAl a) pretreated in H₂ at 250 °C and B) aged catalysts. Reaction feed: 300 ppm NO, 300 ppm CO, 300 ppm C₃H₆, 2000 ppm H₂, 100 ppm C₁₀H₂₂, 10% CO₂, 10% O₂, 5% H₂O, He balance, GHSV = 50,000 h⁻¹.

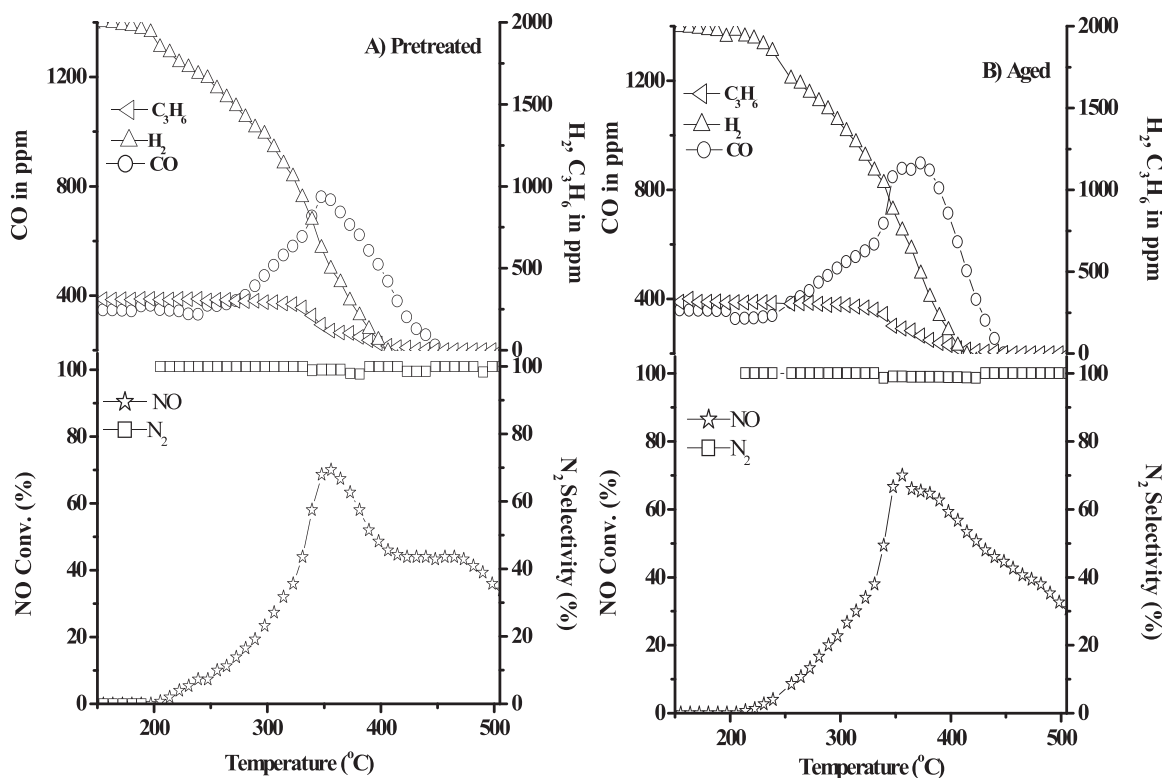


Fig. 6. Change in concentration of CO, H₂ and C₃H₆ and NO_x conversion during HC-SCR on AuAl (A) pretreated in H₂ at 250 °C and (B) aged catalyst. Reaction feed:- 300 ppm NO, 300 ppm CO, 300 ppm C₃H₆, 2000 ppm H₂, 100 ppm C₁₀H₂₂, 10% CO₂, 10% O₂, 5% H₂O, He balance, GHSV = 50,000 h⁻¹.

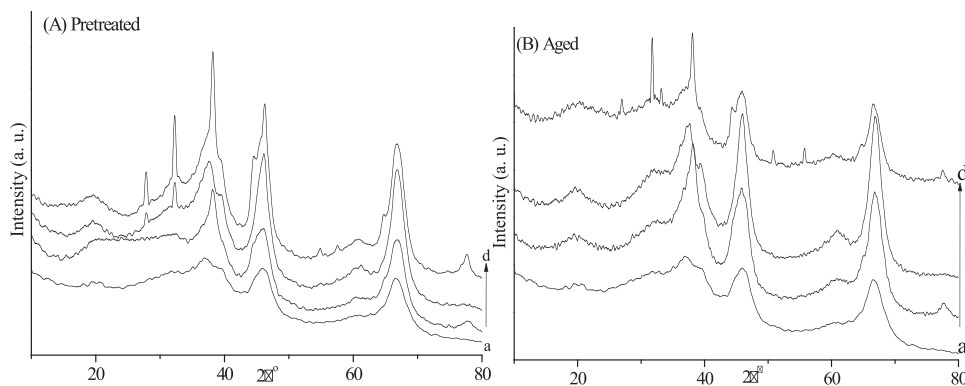


Fig. 7. XRD patterns of a) Al_2O_3 b) AuAl c) AgAl d) AgAuAl catalysts after A) pretreatment in H_2 at 250°C and B) ageing.

Similar features were observed for monometallic AgAl catalyst and are reported in Fig. 5. The formation of H_2/CO with AgAl catalyst pretreated in H_2 at 250°C was observed at temperature of maximum NO conversion though it started at lower temperature (from 250°C). It should be mentioned that at lower temperature upto $\sim 250^\circ\text{C}$ the selectivity for N_2 was not 100% and additional formation of N_2O was observed. Maximum NO conversion of 96% was obtained at 375°C for the catalyst after reduction at 250°C (Fig. 5A). At higher temperature CO concentration increased upto 1073 ppm at 500°C , indicating lower efficiency of AgAl for CO SCR of NO_x . When the same catalyst was aged under reaction feed at 500°C (Fig. 5B), the maximum conversion decreased to 83%. However there was no change in the NO conversion profile at lower temperature up to 350°C . At 500°C the CO concentration was 873 ppm for aged catalyst which could reflect lower extent of decane reforming after ageing procedure. Decrease in NO conversion and CO formation again point out at slight deactivation of the catalyst during ageing procedure. Presence of CO at high temperature in pretreated and aged catalyst indicated that CO was not activated on silver. Hence the formation of CO at high temperature on AgAuAl catalyst can be attributed to the presence of silver.

However in case of AuAl catalyst (Fig. 6) the two major differences were observed. The formation of H_2 through steam reforming at the maximum NO conversion was not evidenced on monometallic AuAl catalyst as it was previously observed in the case of AgAl and AgAuAl catalysts. The formation of small amount of CO on AuAl may be due to partial oxidation of hydrocarbon. At high temperature the successive oxidation of decane to CO and CO to CO_2 or the selective catalytic reduction of NO_x by CO could be suggested. The CO concentration was only around 90 ppm at 500°C underlining the fact that AuAl catalyst was more efficient to activate CO at high temperature. It is also interesting to note that there was no deactivation of AuAl after ageing unlike AgAl or AgAuAl. The maximum NO conversion (70%) as well as temperature of maximum activity (350°C) was unaltered after ageing. In fact there was improvement in high temperature activity after ageing. At 400°C NO conversion increased from 49% to 59% after ageing.

When catalytic performances of bimetallic AgAuAl catalyst was compared with monometallic AgAl and AuAl catalysts, the participation of both gold and silver was evidenced from the concentration profile of the reductants. Complete selectivity for N_2 at lower temperature could be attributed to presence of gold whereas presence of silver could be involved in the steam reforming at higher temperature ($>230^\circ\text{C}$). In case of monometallic catalyst a slight deactivation was observed after ageing (NO conversion decreased from 100 to 83% in case of AgAl catalyst). However no such deactivation due to ageing was evident in case of bimetallic AgAuAl catalyst, in fact there was improvement in low temperature activity (40% NO conversion at 222°C). This suggests slight modifications

of Au and/or Ag nanoparticles during the ageing procedure resulting in formation of more catalytically active Ag and Au species which led to increase in catalytic activity. Moreover the increase in NO conversion at low temperature with complete selectivity for N_2 suggested that gold could be responsible for improved silver dispersion after ageing in case of bimetallic AgAuAl catalyst. Generally the diesel engine exhaust temperature does not exceed 500°C . However during regeneration of diesel particulate filter (DPF) the temperature may exceed 500°C . Hence AgAuAl catalyst was aged at 650°C instead of 500°C in reaction feed for 12 h to test the catalyst stability at high temperature. The SCR activity of AgAuAl catalyst after ageing at 500 or 650°C was similar with respect to NO conversion and N_2 selectivity confirming the high temperature stability of the AgAuAl catalyst.

3.2. Catalyst characterisation

3.2.1. Specific surface area and powder X-ray diffraction analysis

The alumina support prepared by sol-gel method using aluminum tri-sec-butoxide as precursor showed very high specific surface area ($450\text{ m}^2/\text{g}$) (Table 1) compared to conventionally prepared alumina by calcination of boehmite ($237\text{ m}^2/\text{g}$) [15]. The slow hydrolysis of aluminum tri-sec-butoxide led to the formation of semi transparent gel which after drying and calcination gave very high surface area. The specific surface area of the catalyst decreased after deposition of 1 wt% Au (AuAl), 1 wt% Ag (AgAl) or both 1 wt% Au and 1 wt% Ag (AgAuAl). Surprisingly the specific surface area of AgAuAl ($240\text{ m}^2/\text{g}$) was higher compared to AuAl ($210\text{ m}^2/\text{g}$), though in AgAuAl silver nitrate was impregnated on AuAl. Agglomeration of Au during calcination could be prevented due to the presence of Ag in AgAuAl catalyst leading to slightly higher specific surface area of final calcined catalyst compared to AuAl. The lower surface area of AuAl could be due to the agglomeration of Au during calcinations which is otherwise prevented in bimetallic AgAuAl. Table 1 shows elemental analysis of Ag and Au in AgAuAl, AgAl and AuAl catalysts pretreated in H_2 at 250°C which is in agreement with the preparation. EDS results of AgAuAl indicated more availability of silver compared to gold on the catalyst surface. Arve et al. [14] have reported that bimetallic Ag-Au/ Al_2O_3 catalyst with less amount of Au on the surface compared to Ag shows better NO conversion to N_2 .

The XRD patterns of the catalysts pretreated in H_2 at 250°C (Fig. 7A) and after ageing overnight in the reaction feed at 500°C (Fig. 7B) were recorded to study the effect of thermal treatment on the structure of the catalyst. The broad XRD peaks (Fig. 7A-a) observed at 2θ 32.2° , 38.01° , 46.02° , and 66.7° confirmed formation of $\gamma\text{-Al}_2\text{O}_3$ (JCPDS, 29-0063). The broad and low intensity peaks indicated a low crystallinity and high surface area material in agreement with the BET measurements. The XRD pattern of AgAl catalyst

Table 2
Binding energy of Ag and Au in AgAuAl catalyst.

Catalyst	Binding energy (eV.)	% Surface atomic composition (relative accuracy $\pm 20\%$)			
		Au4f _{7/2}	Ag3d _{5/2}	Au (%)	Ag (%)
AgAuAl	Fresh	84.0	368.2	<0.1	0.14
	Aged	83.7	367.9	<0.1	0.27

showed peaks (Fig. 7A–c) at 2θ 38.2, 44.2, 64.4° corresponding to metallic silver (JCPDS, 04-0783). Metallic gold crystallites were detected on AuAl catalyst with characteristic XRD peaks (Fig. 7A–b) at 2θ 38.18, 44.39, 64.57° (JCPDS, 04-784). However peaks of metallic Ag and Au could not be easily differentiated in case of AgAuAl catalyst due to high dispersion of metals as well as overlapping peaks of Ag and Au at 2θ 38.2, 44.2, 64.4° with peaks of γ -Al₂O₃ due to the small difference in *d*-spacing. In case of AgAuAl (Fig. 7A–d) peaks appeared due to the formation of metallic Ag and Au at 44.4 and 64.5° as shoulder with broadening of alumina peak at 46.02 and 66.7° , respectively. The XRD patterns of all the catalysts after ageing in reaction feed a 500 °C are given in Fig. 7B. After ageing monometallic catalysts (AgAl and AuAl) showed similar characteristics as that of pretreated. In case of bimetallic AgAuAl catalyst (Fig. 7B–d) the broadening of the peaks was observed after ageing with significant decrease in peak intensity. The broadening suggested a better dispersion of silver and gold particles on alumina support with formation of smaller metallic particles.

3.3. Characterisations of pretreated and aged catalysts

Effect of various pretreatments and ageing on the dispersion of metals on alumina surface as well as formation of different metallic species on the surface was studied by detailed bulk and surface characterization of the pretreated and aged catalysts.

3.3.1. UV–vis diffuse reflectance spectroscopy study

A UV–vis diffuse reflectance spectrum of AgAuAl catalyst after various pretreatments is shown in Fig. 8. For clarity in distinguishing the peaks for different species of active component, UV spectrum of Al₂O₃ was subtracted from UV of all the catalyst samples. AgAuAl catalyst after pretreatment in H₂ at 250 °C (Fig. 8a) showed bands at 450 nm and 525 nm corresponding to the metallic silver and gold, respectively. The presence of Ag_n^{δ+} clusters was evidenced by the band at 275 nm [16,19,24–31]. The pretreatment in presence of H₂ at 500 °C (Fig. 8b) has led to change in the UV–vis spectra with the decrease in the contributions at 550 nm and 275 nm. Decrease in intensity of band at 275 nm suggested the decrease in concentration of Ag_n^{δ+} species due to complete reduc-

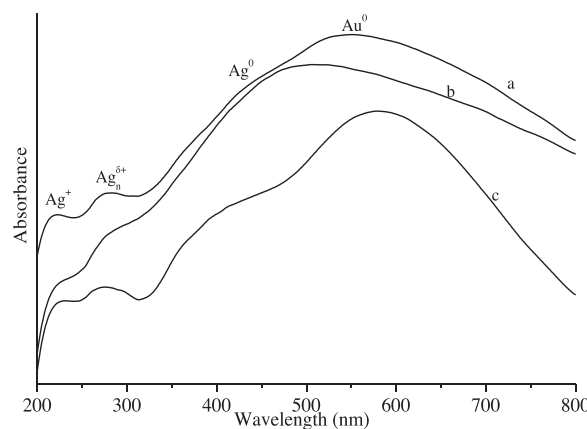


Fig. 8. UV–vis DRS spectra of AgAuAl catalyst pretreated in a) 250 °C in H₂, b) 500 °C in H₂, c) 500 °C in air.

tion to metallic silver. Also band at 490 nm corresponding to the AgAu alloy was observed, indicates that high temperature pretreatment under H₂ (500 °C) led to the formation of alloy, which was not observed after reduction at 250 °C. A shift was observed in metallic silver (450 nm) and gold (525 nm) bands when AgAuAl catalyst was pretreated in presence of air at 500 °C (Fig. 8c). Clearly the nature of Ag and Au particles was significantly modified by the pretreatment. The intensity of Ag_n^{δ+} band was maximum when AgAuAl catalyst was pretreated in H₂ at 250 °C indicating formation of more Ag_n^{δ+} clusters compared to other pretreatments.

The comparison of UV–vis spectra of AgAuAl, AgAl and AuAl catalysts after pretreating in presence of H₂ at 250 °C is presented in Fig. 9A. The intensity of band at 275 nm was significantly higher for AgAuAl catalyst compared to AgAl catalyst, indicating higher concentration of Ag_n^{δ+} species. AgAl catalyst also showed the presence of Ag⁺ at 230 nm. The metallic silver was observed at 450 nm in AgAl as well as AgAuAl catalysts. The large metallic Ag clusters are reported to lead to the formation of N₂O at low temperature in HC-SCR using Ag/Al₂O₃ catalyst [32]. Hence in present case also the formation of N₂O at low temperature (below 250 °C) on AgAl catalyst (Fig. 5A) can be attributed to larger silver particles whereas in case of AgAuAl catalyst no N₂O formation was observed. Arve et al. have also reported 100% selectivity for N₂ using bimetallic Ag–Au system [14]. Both AuAl and AgAuAl catalysts showed presence of metallic gold at 554 and 550 nm, respectively [19,26,28–31]. There was no AuAg alloy formation observed in UV (band at 460–490 nm) after reduction at 250 °C.

The effect of ageing in reaction feed at 500 °C was studied by UV–vis DRS for all the catalysts after pretreating in presence of H₂ at 250 °C (Fig. 9B). The intensity of Ag_n^{δ+} species (275 nm) increased

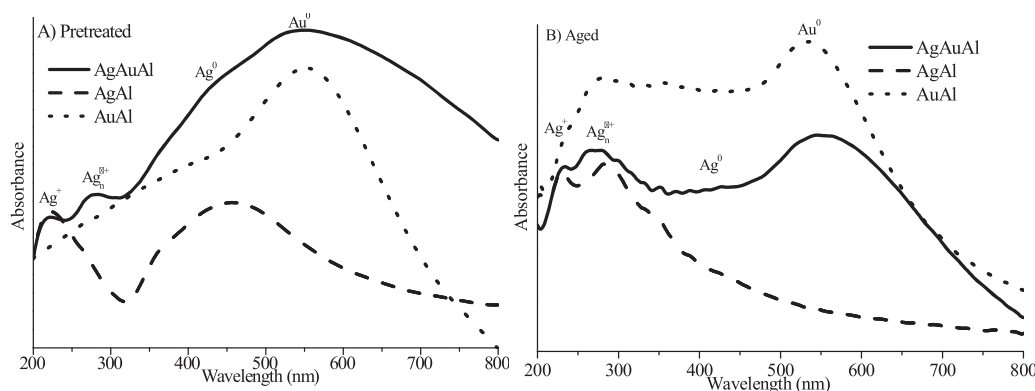


Fig. 9. UV–vis DRS spectra of AgAuAl, AgAl and AuAl catalysts after A) pretreatment in H₂ at 250 °C and B) aged.

considerably on aged AgAuAl catalyst compared to pretreated catalyst. At the same time the band corresponding to the metallic silver (450 nm) disappeared. There was no change in band position of metallic gold (550 nm) after ageing indicating no agglomeration of gold particles due to ageing at 500 °C. The band related to $\text{Ag}_n^{\delta+}$ species developed in case of aged AgAl catalyst at the expense of the band corresponding to the metallic silver which confirmed the oxidation of metallic silver to $\text{Ag}_n^{\delta+}$ (through Ag^+) during ageing procedure. The Ag^+ species may get converted to $\text{Ag}_n^{\delta+}$ clusters in presence of H_2 and O_2 [24]. AuAl catalyst showed shift in peak maxima for metallic gold to lower wavelength (554–534 nm) after ageing which suggested an improved dispersion of Au particles with corresponding decrease in particle size.

Increase in the relative concentration of $\text{Ag}_n^{\delta+}$ species in AgAuAl catalyst after ageing could be due to the presence of H_2 , O_2 and hydrocarbon in the reaction feed [33]. H_2 and O_2 can adsorb dissociatively to form $-\text{OH}$ species ($\text{Ag}-\text{OH}$). In case of $\text{Ag}-\text{OH}$ formation a transfer of charge from Ag to OH was proposed in the literature accompanied by back donation from OH to Ag (Ag^+). The extent of charge transfer from Ag to OH is greater than the charge transfer from OH to Ag^+ leading to the formation of $\text{Ag}_n^{\delta+}$ [27,24]. Similarly in present study also the $\text{Ag}_n^{\delta+}$ formation in AgAl may be proposed from Ag^0 via Ag^+ . Partially charged metallic silver and metallic gold were clearly observed in UV–vis DRS analysis and could influence the SCR of NO_x [4–5,14–15,18,19,26,22].

3.3.2. XPS studies

Fig. 10 shows the comparison of XPS data for pretreated and aged AgAuAl catalyst plotted on the common scale of intensity. Table 2 summarises the binding energy as well as surface concentration of Ag and Au on AgAuAl catalyst. The catalyst reduced at 250 °C showed considerably lower intensity of silver species compared to aged catalyst on the surface (Fig. 10). XPS data clearly revealed increased intensity of silver species on aged catalyst compared to pretreated AgAuAl catalyst. The BE for Ag^+ was observed at 367.15 eV in pretreated AgAuAl catalyst which remained almost unchanged after ageing, however the BE for Ag^0 was observed at 368.6 eV which shifted to 368.5 eV after ageing. The ratio of Ag^0/Ag^+ was calculated to be 3.95 for pretreated AgAuAl catalyst which changed to 2.25 after ageing clearly indicating decrease in Ag^0 species due to ageing which is in well agreement with UV results where the peak corresponding to Ag^0 at 450 nm diminished after ageing. The UV spectrum of the sample after subtraction of alumina also showed formation of more $\text{Ag}_n^{\delta+}$ species after ageing. The surface silver concentration calculated from XPS was found to be 0.14 for catalyst pretreated in H_2 at 250 °C which increased to 0.27 after ageing in reaction feed at 500 °C confirming increased surface con-

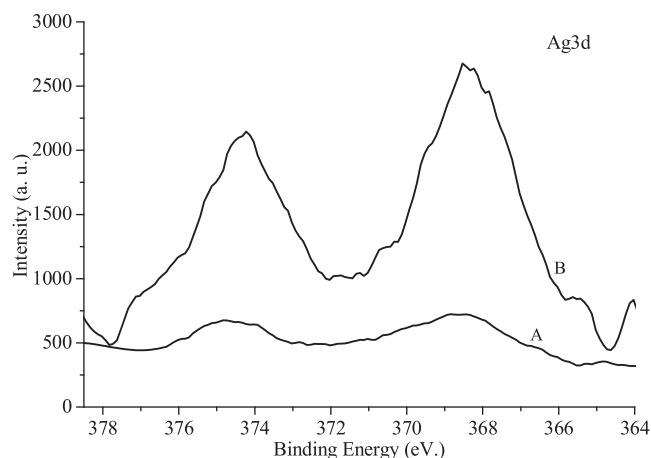


Fig. 10. Comparison of XPS spectra of AgAuAl catalyst after (A) pretreatment in H_2 at 250 °C and (B) aged.

centration of silver species after ageing. Hence, the XPS and UV–vis data is in agreement with catalytic activity data.

This indicated a reorganisation of the silver species on the surface due to ageing generating more number of silver species available on the surface. This has led to the improved catalytic activity of AgAuAl catalyst after ageing. Nam and colleagues [34] have reported improved low temperature SCR activity of $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst due to increase in concentration of various silver species on the surface. The XPS data has been deconvoluted in Fig. 11. AgAuAl catalyst reduced at 250 °C (Fig. 11A) showed peaks at 368.8 and 367.1 eV, corresponding to Ag^0 and Ag^+ species, respectively [35]. The Ag $3d_{5/2}$ photopeaks shifted to lower binding energy after ageing (Fig. 11B) from 368.8 eV to 368.5 eV. The initial binding energy value of Ag $3d_{5/2}$ photopeak at 368.8 eV indicated partial oxidation of silver species. This shift may be attributed to the formation of higher number of $\text{Ag}_n^{\delta+}$ species which is in agreement with UV results as shown in Fig. 9 [22]. However there was no detectable shift observed for the peak at 367.1 eV for Ag^+ after ageing. Sato et al. [16] have reported $\text{Ag}_n^{\delta+}$ cluster to be responsible for the formation of isocyanate species which are key intermediate in NO_x reduction reaction.

3.3.3. EDS studies

The metal dispersion after pretreatment and ageing was studied by elemental mapping of catalysts in $7.5 \times 7.5 \mu\text{m}^2$ area (Fig. 12). Energy dispersive X-ray spectroscopic analysis of AgAuAl catalyst indicated higher density of silver spots than gold. This suggested

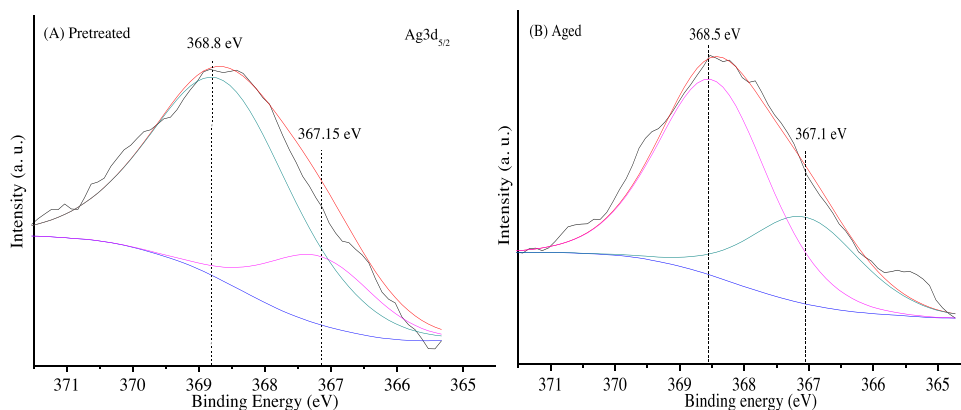


Fig. 11. Deconvoluted Ag $3d_{5/2}$ photopeak of AgAuAl catalyst after (A) pretreatment at 250 °C in H_2 and (B) ageing.

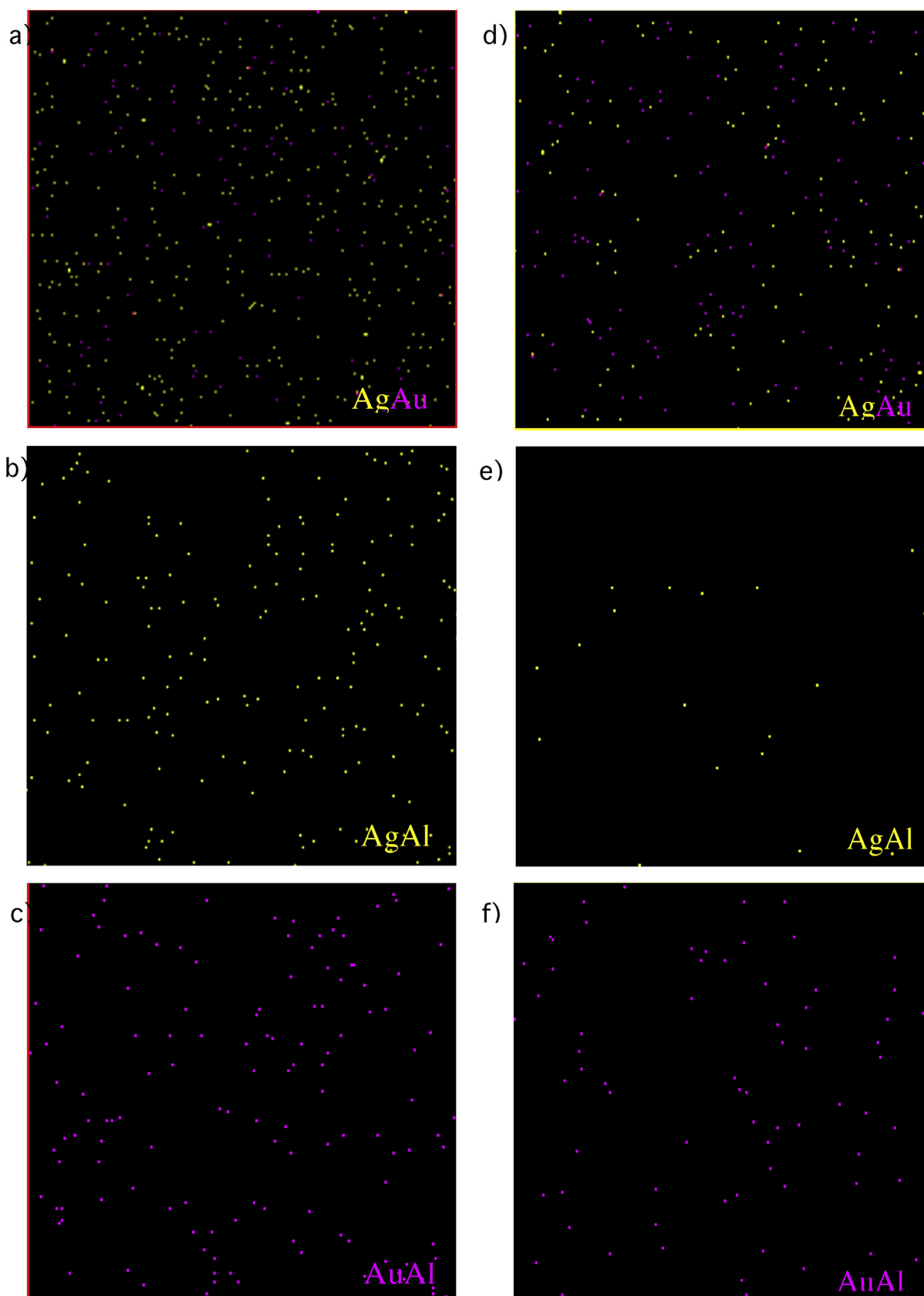


Fig. 12. Elemental mapping ($7.5\ \mu\text{m} \times 7.5\ \mu\text{m}$) images of catalysts after pretreatment at 250 °C in H₂ of: a) AgAuAl b) AgAl c) AuAl and after ageing: d) AgAuAl e) AgAl f) AuAl.

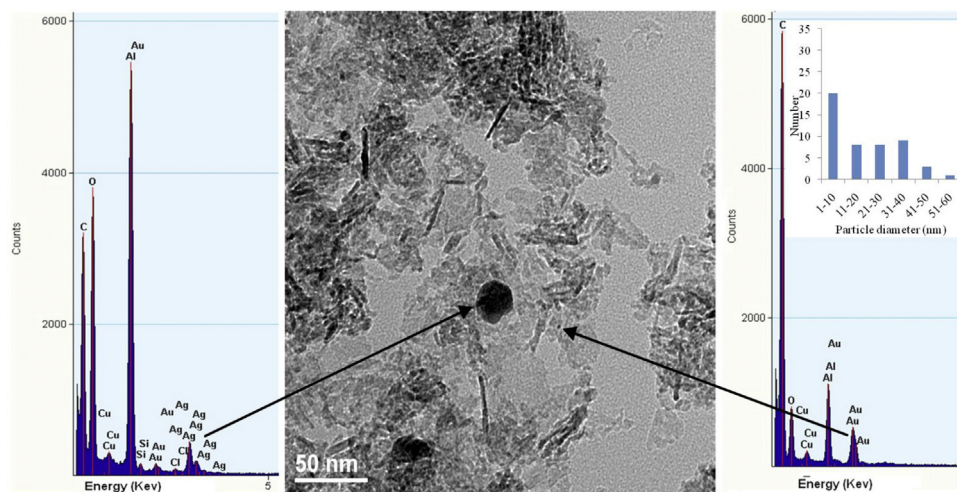


Fig. 13. TEM image, spot EDS and particle size distribution (inset) of AgAuAl catalyst pretreated in H_2 at 250 °C.

more availability of silver particles compared to gold on the catalyst surface. Arve et al. [14] have reported that bimetallic Ag–Au/ Al_2O_3 catalyst with less amount of Au on the surface compared to Ag shows better NO conversion to N_2 . The ageing of monometallic AgAl and AuAl catalyst led to opposite behaviour. The density of Au spots decreased marginally whereas the density of Ag spots decreased significantly. This behavior was in agreement with the evolution of the catalytic performances after ageing. Bimetallic AgAuAl catalyst showed improved dispersion of silver and gold particles compared to freshly pretreated catalysts. The ageing of AgAuAl catalyst gave rise to a slight decrease of spots related to Ag and Au. The stabilization of silver particles in the presence of gold was then suggested according to EDS analysis. As elemental mapping by EDS analysis gives only metal dispersion and not particle size of the elements, further TEM analysis was carried out to determine the particle size of Ag and Au before and after ageing.

3.3.4. Transmission electron microscopy analysis

TEM images and particle size distribution of pretreated and aged AgAuAl catalyst is presented in Figs. 13 and 14, respectively. AgAuAl catalyst after pretreatment in H_2 at 250 °C showed presence of well

dispersed silver and gold particles on alumina surface. The larger particles (>20 nm) were found to be of silver whereas smaller particles (<10 nm) were found to be of gold as analysed by spot EDS analysis (Fig. 13 inset). Haruta and colleagues [9] have shown that Au/ Al_2O_3 prepared by deposition precipitation method gives Au particles of 4–5 nm whereas wet impregnation method leads to Au particles of 32 nm. After ageing the particle size distribution showed gold particles to be in the range of 1–10 nm. However the particle size of silver after ageing was found to be smaller than that of pretreated catalyst. The TEM images of AgAuAl catalyst showed well dispersed silver and gold nanoparticles with uniform distribution on the surface which is in well agreement with the XRD and EDS results. Bukhtiyarov and Kaichev [36] demonstrated that silver particles greater than 30 nm forms nucleophilic oxygen. Thompson and Hodnett [37] have reported nucleophilic oxygen to be responsible for the mild oxidation of hydrocarbon. Hence in present study it can be proposed that adsorbed nucleophilic oxygen on silver species can partially oxidise decane to assist further reforming reaction which in turn improves the SCR activity.

The characterisation data can be correlated to the improved SCR activity of bimetallic AgAuAl catalyst compared to corresponding monometallic AgAl and AuAl catalysts. The high specific surface area of alumina support (450 m^2/g) prepared by sol–gel method can favor high dispersion of active metals on the surface especially for gold nanoparticles. UV–vis characterisation of AuAl catalyst showed a shift in peak maxima for metallic gold to lower wavelength (554–534 nm) after ageing suggesting an improved dispersion of Au particles with corresponding decrease in particle size. This could be responsible for enhanced NO conversion at higher temperature after ageing on AuAl catalyst. Gold particles of 1–20 nm are reported to be active for NO_x reduction [9,20].

On AgAuAl catalyst, several characterisations especially UV–vis confirm the formation of Ag^+ and $Ag_n^{\delta+}$ species which are known for high NO conversion. $Ag_n^{\delta+}$ is proposed to be responsible for high SCR activity at low temperature whereas well dispersed Au particles are known for high temperature activity. The maximum number of $Ag_n^{\delta+}$ clusters were observed in AgAuAl catalyst when pretreated at 250 °C in presence of H_2 , resulting in higher activity compared to other pretreatments at 500 °C in air and H_2 . UV–vis spectroscopy also underlined the higher intensity of band at 275 nm for AgAuAl catalyst compared to AgAl, indicating higher concentration of $Ag_n^{\delta+}$ species which is in agreement with the higher SCR activity observed as shown in Fig. 3B. AgAuAl and AgAl showed increase in low temperature activity after ageing under reaction feed which could be due to the maximum dispersion of

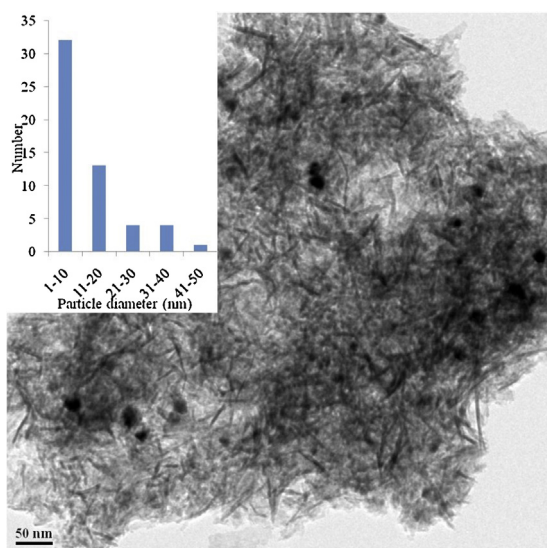


Fig. 14. TEM image and particle size distribution of AgAuAl catalyst aged in reaction feed.

$\text{Ag}_n^{\delta+}$ species supported by the UV and EDAX data. The slight decreases in activity with concomitant decrease in formation of CO indicate the increased oxidative nature of surface Ag species. AuAl catalyst showed increase in CO concentration after ageing above 350 °C indicating increase in partial oxidation of hydrocarbon which could be due to the change in redox properties of gold. The increase in intensity of XPS peaks (Fig. 10) for silver species as well as increase in $\text{Ag}_n^{\delta+}$ related contribution (UV) after ageing could be related to the high activity of AgAuAl catalyst after ageing. The significantly improved metal dispersion in case of AgAuAl, AgAl and AuAl catalysts after ageing as evidenced by EDS analysis could also be related to improved low temperature activity in case of AgAuAl and AgAl catalysts whereas improved high temperature activity in case of AuAl. Hence in present case AgAuAl catalyst with lower gold content compared to silver on surface could be optimal for optimizing the catalytic activity for hydrocarbon SCR.

4. Conclusion

Bimetallic catalyst Ag–Au supported on high surface area alumina prepared by successive impregnation method has shown high SCR activity when pretreated in hydrogen at 250 °C. The performance of bimetallic AgAuAl catalyst was better when pretreated at 250 °C in H_2 compared to pretreatment at 500 °C in H_2 or air. The SCR activity further improved (94% NO conversion at 382 °C) after ageing at 500 °C in reaction feed. The SCR activity of bimetallic AgAuAl catalyst was higher compared to corresponding AuAl and AgAl catalysts after ageing. The SCR activity of AgAuAl catalyst did not decrease even after ageing the catalyst at 650 °C in reaction feed indicating high temperature stability of the catalyst. The higher activity of bimetallic AgAuAl catalyst for NO reduction after ageing has been correlated to the formation of well dispersed $\text{Ag}_n^{\delta+}$ clusters and small metallic gold particles on alumina support as confirmed by various characterisation techniques. Detailed characterisation revealed modification of the catalyst surface by improved silver dispersion and hence metal support interaction after ageing which led to enhanced low temperature activity of bimetallic catalyst. Improved activity of AgAuAl catalyst can also be attributed to steam reforming reaction which was confirmed by formation of CO at the temperature of highest activity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.02.035>.

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